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# **Temporal trends of elements in Turin (Italy) atmospheric particulate matter from 1976 to 2001**

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## **Abstract**

The temporal trends of major, minor and trace elements in the total atmospheric particulate sampled in the urban area of Turin (Italy) were determined for the following years: 1976, 1986, 1996 and 2001. The wavelength dispersive X-ray fluorescence (WD-XRF) technique was adopted to determine the concentrations of Ba, Br, Ca, Cl, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, S, Ti and Zn. A smaller number of samples was also analyzed by ICP atomic emission spectroscopy (ICP-AES) and the results were compared with those obtained by WD-XRF to confirm their validity. A clear seasonal pattern with higher concentrations of the aforementioned elements in the cold periods was observed. Moreover, a change in the chemical composition of atmospheric particulate matter was evidenced, particularly between the first (1976 and 1986) and the last (1996 and 2001) years. This change can be attributed both to the greater contribution of Pb and Br to atmospheric pollution in the past and, in recent years, to the higher level of pollutants associated with increased vehicular traffic and industrial activities. The application of chemometric techniques (Principal Component Analysis and Cluster Analysis) allowed us to speculate about the main emitting sources influencing the total atmospheric particulate in these years.

## **Keywords**

TSP; Turin (Piedmont Region, Italy); Elements in TSP; Enrichment Factors; Pattern Recognition

## **1. Introduction**

Epidemiological studies have shown that the exposure to atmospheric particulate matter in urban areas has the potential to affect the health of the local community, causing various respiratory tract pathologies (allergies, asthma, lung emphysema) and cardiopulmonary mortality (Donalson et al., 2002; Englert, 2004; Stone, 2000).

Atmospheric particulate matter (PM) is a complex mixture of inorganic and organic substances comprising inert carbonaceous cores with multiple layers of materials including metals, organic vapors, acid salts and biological compounds such as endotoxins, allergens and pollen fragments (Spurny, 1996).

Particle size and composition are key properties responsible for the impact on human health. Urban PM has been found to contain significantly high amounts of metals, which constitute a likely cause of the health-related effects of PM, as demonstrated by a number of studies (Burnett et al., 2000; Zelikoff et al., 2002; Zereini et al., 2005).

Atmospheric particulate matter is routinely collected on filters and analyzed gravimetrically and/or by chemical analysis. As to the inorganic components of PM, several techniques are available for

compositional analysis, including atomic absorption spectroscopy (AAS), inductively coupled plasma-atomic emission spectroscopy (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS) and voltammetry (Buzica et al., 2006).

For these techniques the analysis of PM filter samples requires a time-consuming digestion that may alter the elemental composition of the sample by contamination or losses. Current European Directives concerning air pollution (European Council-Directive, 1999; European Council-Directive, 2004) have established reference methods for heavy metals, including graphite furnace atomic absorption spectroscopy (GF-AAS) and ICP-MS (European standard, 2005). However, other methods may be used if they yield equivalent results.

Wavelength dispersive X-ray fluorescence (WD-XRF) is a promising technique for environmental analysis and it has been reported as an alternative technique to monitor PM composition (Talebi, 1998; Vázquez et al., 2005). This technique allows the direct analysis of PM filters. In this work we confirm that WD-XRF is a suitable alternative to standardized methods for PM filter analysis. Unnecessary digestion makes WD-XRF competitive to other techniques such as AAS and ICP. Moreover, being non-destructive it allows measurements repetition and/or further sample investigations.

Several studies have been carried out identifying, characterising and quantifying sources of PM in Europe (Alleman et al., 2010; Viana et al., 2008; Yin et al., 2005). Concerning Piedmont, Italy, only few research studies on particulate matter have been reported (Casale et al., 2009; Migliaretti et al., 2007).

In the last decades, attention has been focused on the finest particulate fractions (PM<sub>10</sub> and, recently, PM<sub>2.5</sub> and PM<sub>1</sub>), since they were recognized as the most harmful to human health owing to their higher probability of deposition deep in the respiratory tract. In earlier periods, Total Suspended Particulate (TSP) was investigated. TSP filters were used at the sampling stations within the city of Turin, Piedmont Region, up to 2000. Since 2001 the regional agency for environmental protection (ARPA Piemonte) has been gradually replacing gravimetric samplers for TSP with those for PM<sub>10</sub> – PM<sub>2.5</sub>. ARPA Piemonte is therefore in possession of a series of TSP samples collected on glass fiber filters from 1976 to 2001.

In this study we determined the contents of 15 elements in TSP filters collected at two sampling sites in Turin, one localised in the centre and the other in the outskirts of the town, for the years 1996 and 2001 and 1976, 1986, 1996 and 2001 respectively. The goals of the investigation are to identify the main sources affecting this urban area, their seasonal pattern and the evolution of their impact on ambient air quality in the aforementioned periods. At this aim, we have calculated the

crustal enrichment factors (EF) for the elements investigated and we have used principal component analysis (PCA) and cluster analysis (CA).

To our knowledge, a few studies report the concentrations of inorganic components in atmospheric particulate matter for a broad time span, therefore our study can be useful to gain insight into the temporal evolution of the composition of airborne particulate matter and its possible relationships with changes in anthropic activities.

## **2. Experimental**

### **2.1 Site description**

Turin is a large town characterised by a high density of residential and commercial premises and a very high volume of vehicular traffic; many industries, including power plants, chemical plants, plastic and metallurgical factories are located on the outskirts.

TSP samples were collected in two different sites: one site, called TO1, is localised in the historical centre (Via Della Consolata); the other one, called TO2, is in the Northern suburbs (Piazza Rebaudengo), in an area subject to intense vehicular traffic (Figure 1). During the study period, in the Turin historical centre there were still coke or oil-fired heating systems although most of the city heating systems use natural gas.

### **2.2 Sample collection**

A total of 72 glass fiber filters, 24 from TO1 (one per month for 1996 and 2001), and 48 from TO2 (one per month for 1976, 1986, 1996 and 2001) were analyzed. The filters have a total diameter of 47 mm and a nominal surface deposit diameter of 38 mm. We have considered the TSP samples that fall between the 5° and 95° percentile calculated on the TSP concentrations for each year. Subsequently, for each month, those samples having the highest quantity of particulate were chosen for analysis.

### **2.3. Sample analysis**

All filters had previously been analysed to determine the mass of particulate collected using a gravimetric technique (Lawless and Rodes, 1999).

The filters were analysed for total element concentrations using a Rigaku ZSX wavelength dispersive X-ray fluorescence spectrometer (WD-XRF). The following crystals functioning as diffracting elements are present in this instrument: LiF, Ge, PET, TAP; so it is possible to determine Ba, Ca, Cl, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, S, Ti and Zn.

The filters were placed on the sample holder and directly analyzed. The filter blank was analysed by the same procedure to evaluate its contribution in the sample analysis: it was evidenced that Na, Sr, Al, Si and P were not quantifiable using XRF because of the too high filter blank contributions.

The metal contents present in the filters sampled in 1976 at TO2 site were also determined with a Varian Liberty 100 ICP atomic emission spectrometer (ICP-AES). An acid digestion in a Milestone MLS-1200 Mega microwave oven was chosen as the dissolution procedure. The filters were cut into two equal parts, which were weighed and treated with 5 ml of aqua regia in polytetrafluoroethylene (PTFE) bombs. Four heating steps of 5 min (250, 400, 600, 250W respectively) were applied. The resulting solutions were filtered and diluted to 30 ml with Milli-Q (Millipore) ultrapure water (18.2 MΩ cm). Nitric and hydrochloric acid were purified by sub-boiling distillation.

Three replicate measurements were made to determine the average concentration and standard deviation for each analysis. The calibrations were performed with standard solutions prepared in aliquots of sample blanks. Process blanks were incorporated into the dissolution and analytical procedure to assess metal contribution from the filters, bombs, Milli-Q water and purified acids used for the dissolution.

NIST SRM 1649a (urban dust) was used to verify that analyte concentrations were within 10% of the expected values before proceeding with sample analysis.

### **3. Results and Discussion**

#### *3.1. Comparison of XRF and ICP-AES*

To compare results obtained by XRF and ICP-AES, linear regression was conducted, and scatter plots of the amount of Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Pb, Ti and Zn, measured from each filter, were constructed. It was not possible to determine the concentrations of Br, Cl, Ni and S by ICP-AES because their concentrations were lower than detection limits. The repeatability of XRF and ICP-AES methods was similar ( $RSD = \pm 2\%$ ) for all elements with the exception of K and Mg (for XRF,  $RSD = \pm 5\%$ ). These values can be considered satisfactory and show that both methods are suitable for TSP analysis from the point of view of precision.

The comparison (Figure 2) indicates relatively good agreement between the amounts of Ba, Cr, Cu, Fe, K, Mn, Pb, Ti and Zn determined by XRF and ICP-AES. The amounts of Ca, Mg, Mn and Ti determined by ICP-AES were consistently lower than those determined by XRF as demonstrated by the values of the slopes, which were always lower than 1. The most likely explanation for this discrepancy is the incomplete dissolution of these elements from filter samples in the digestion step. The correlation coefficients  $r$  suggest that the amounts of Ba, Cr, Cu, Fe, K, Mn, Pb, Ti and Zn can

be reliably determined by either analytical method, whereas the preferable method for determining the amounts of Ca and Mg will need validation through comparison with another analytical method. In particular the intercept and the slope of the linear regression (at the 95 % confidence level) for Cr, Cu, Mn and Ti are close to 0 and 1, respectively, indicating that the two analytical methods give similar results for these analytes.

The sensitivity of the proposed WD-XRF technique allowed us to determine a number of elements in PM. Furthermore, the principal advantage of this method over ICP-AES is that it is reliable but non-destructive, so that the filters can be archived for further investigations.

The advantages of this procedure are hence evident: 1) simultaneous multi-elemental analysis; 2) the measurement is easy to perform and rapid; 3) samples are not destroyed by time-consuming digestion procedures, then protected filters can be stored; 4) any risk of diluting the sample below detection limits is avoided; 5) the procedure is reliable.

However, WD-XRF has some disadvantages in comparison with other techniques: 1) overlapping peaks may complicate the quantification of some elements, when their surface concentration is very low; 2) the matrix effect may be high, hindering the quantification of some elements; 3) different crystals are necessary to analyse a large number of elements; 4) detection limits are usually higher than those of ICP-AES or GF-AAS.

### *3.2. Chemical composition, temporal trends*

The mean and median concentrations as well as the minimum and maximum values of the elements analysed are shown in Table 1 for all the years considered and both the sampling sites; the results have been reported also distinguishing the warm season (April – September) from the cold season (October – March). Figure 3 shows the temporal trends of element concentrations in TSP samples.

The overall mass of the analysed elements is, on average,  $19 \pm 2$  % of the TSP mass concentration; the low standard deviation indicates that the total element to TSP ratio does not change either with time or from one site to the other.

Comparing lead concentrations with the acceptable limit imposed by the European Directive 1999/30/EC ( $0.5 \mu\text{g}/\text{m}^3$ ), it is evident that they are always lower than this limit. Nickel concentrations exceed the target value ( $20 \text{ ng}/\text{m}^3$ ) reported in the European Directive 2004/107/EC in 1996 and 2001. It must be borne in mind that high Ni levels ( $110 - 180 \text{ ng}/\text{m}^3$ ) have been recorded in other heavily industrialised areas and large cities (Prodi et al., 2009; WHO Regional Publications, 2000). The higher Ni concentration in the last two years is likely due to the presence of new or stronger anthropogenic sources, especially combustion processes.



Figure 3 shows a clear seasonal pattern of analyte concentrations, with higher levels of all the elements in the cold season. This behaviour has also been observed by other researchers in other sites in Northern Italy (Marcazzan et al., 2001; Prodi et al., 2009). This pattern is mainly dependent on the frequent thermal inversions and ground-level fog during autumn and winter that aggravate the already-poor air quality. These climatic phenomena have a relevant effect, particularly in orographically complex areas such as the Alpine arc surrounding the North-West sector of Piedmont. The stagnation of air in the valley floors, caused by severe thermal inversions in winter, gives rise to an accumulation of all pollutants. In some situations, when the thermal inversion is very strong while the *foehn* winds are weak, air recirculation is limited, resulting in intense urban pollution. This scenario is compatible with the seasonal pattern of TSP composition that shows a greater increase in cold periods of the species mainly related to anthropogenic activities (Cl, Br, S and Pb). The behaviour of Cl could be due to the use of NaCl to prevent ice formation on roads; the levels of Br and Pb are greater in the cold season particularly in 1976 and 1986, reflecting both the use of leaded petrol at the time and the yearly pattern of urban traffic; finally the higher content of S in cold periods is likely for the most part related to emissions from coal and oil-fired heating systems. This last finding is not in agreement with the trend generally found for sulphur, whose concentration in atmosphere is high both during the summer (because of photochemical reactions) and during the winter (because of the high consumption of fossil fuels) (Day et al., 1997); the behaviour observed in our study is likely indicative of the higher contribution of this last source.

Comparing seasonal trends over time, it is evident that most of the elements in TO2 site are characterised by concentrations that clearly increase between the first two and the last two years, namely 1976 – 1986 and 1996 – 2001, with the exception of Pb and Br, having an opposite trend, and S, which maintains similar concentrations in all years; in TO1 site, all elements have higher concentrations in 1996 than in 2001. The explanation for the behaviour of Pb and Br is reported above. The behaviour of S, instead, is difficult to explain; anthropogenic sulphur is usually generated from oil combustion, coal combustion, metal smelting or other human activities: it is possible that different anthropogenic sources have contributed to the atmospheric S concentration over the years and their combined effect results in a constant concentration over time. The increase of the concentrations of all the other elements for TO2 site can be attributed to a greater contribution from several sources: first of all, urban traffic followed by industrial and domestic fossil fuel combustion and steel and power plant emissions. On the whole it is reasonable to suppose that these elements were emitted into the atmosphere by sources changing over time or by the same sources changing their impact over time.

Finally it is interesting to note that element trends in sites TO1 and TO2 for 1996 are very similar both in concentration and seasonal behaviour, whereas for 2001 they are similar in seasonal behaviour but not in the concentration levels since most of the elements, with the exception of Br (no data available for TO2 in 2001), Cl and Pb, are present in higher concentrations in site TO2 than in TO1.

### 3.3 Enrichment Factors

Enrichment Factors (EF) for heavy metals relative to Earth's crustal composition were calculated according to:

$$EF = (C_{Me}/C_{Fe})_{sample} / (C_{Me}/C_{Fe})_{Crust}$$

where  $(C_{Me}/C_{Fe})_{sample}$  is the concentration ratio of the metal and Fe in sample and  $(C_{Me}/C_{Fe})_{Crust}$  is the same ratio in Earth upper-crust as reported by Wedepohl (1995). We used crustal Fe level as a reference since soil is considered to be the major source of Fe in aerosol.

Figure 4 shows the EF results for each year and sampling site as well as for all years and both sampling sites. The interpretation of EFs can be made as follows: elements with EFs up to 10 are not considered to be enriched; elements with EFs between 10 and 100 are rated as moderately enriched; elements having EFs higher than 100 are considered to be highly enriched and have different sources to those of the Earth's crust (Gharaibeh et al., 2010). However, it must be mentioned that EF only provides qualitative information on element sources because of the wide variation in concentrations in the upper crust (Contini et al., 2010). In this case study Pb, Zn, S, Br and Ba are enriched: this is a further indication that they have predominantly a non-crustal origin. The most likely sources for Pb, Br and S were reported above. The probable source for Ba and Zn is vehicular traffic. Cu, Ni, Cl and Cr are moderately enriched and can be considered mainly of anthropogenic origin. Finally Ti, K, Mn, Mg and Ca are not enriched and are mainly of crustal origin (even if some differences exist within this group of elements).

As written above, the values of EFs have been calculated separately by year and sampling site (Figure 4 a) and b)) in order to evaluate both their temporal trends and their behaviour in the two sites. It is interesting to note that, among the high EFs shown in Figure 4b, the highest values were always found for 1976 and 1986.

It is evident, particularly for site TO2, that the elements more closely related to the use of gasoline (Pb and Br) and to coal and oil-fired heating systems (S) are characterised by EFs values decreasing over time. In particular, the decreasing trend observed for sulphur EF might indicate that this element, measured in the atmospheric particulate matter of Turin in 1996 and 2001, was mainly due to secondary sulphates originated on a regional scale from the oxidation of SO<sub>2</sub> primarily emitted

by power plants and industries. Because of the increasing use of methane in recent years, domestic heating in the urban area of Turin contributes less to sulphates.

The trend observed for Cu in site TO2 is similar to that of Pb, Br and S, but its decrease over time is less marked, likely because it is due to a lower impact by industrial sources rather than to a lower contribution by vehicular traffic. Moreover, Figure 4b shows that the EF of chromium and nickel is characterised by a contrasting trend when compared to other enriched elements, i.e. increasing over time; this probably indicates the presence of a new pollution source or the intensification of an existing one, likely related to industrial activity. The EFs of all the other elements remain similar over time.

### *3.4. Chemometric investigation and source identification*

There are several source apportionment techniques (Viana et al., 2008; Watson et al., 2002) requiring different levels of knowledge about the sources acting on a site and their emission profiles. We have used two unsupervised methods: Principal Component Analysis (PCA) and Cluster Analysis (CA).

PCA is a well-established method for aerosol analysis after its first application to aerosol source apportionment (Thurston and Spengler, 1985). Its strength is that it is based on the evolution of data collected in a specific site, and an a priori knowledge about sources is not required. In some cases it may be difficult to extract information from PCA, especially if sources with similar profiles are present, so extra information may be needed to achieve a full interpretation of the data (Prendes et al., 1999). For this reason CA has also been performed. Cluster analysis is an effective statistical method for the qualitative study of atmospheric aerosol composition and can be used to confirm the groups of variables obtained with PCA (Contini et al., 2010; Dongarrà et al., 2007; Miranda et al., 1996). Data elaboration has been performed with XlStat 2007.3 software package.

This chemometric study was carried out considering the analytical data for the two sites both separately and as a total data set (72 samples with 15 variables). All data sets considered were autoscaled separately. For concentrations below the detection limit, a random value between zero and that limit was inserted in order to thoroughly apply PCA and CA without losing any data.

Figure 5 shows the score and loading plots obtained by PCA considering the samples collected in site TO1. The samples are grouped in four clusters: 1) samples TO1-Dec-01 and TO1-Jan-01; this group is greatly influenced by the variable identified by the vector of Cl, characterised by higher concentration in the cold periods for the reasons listed above; 2) sample TO1-Jan-96; this sample is differentiated from all the other ones due to high concentrations in most of the elements considered. It may reflect an exceptional pollution event or a contamination during analysis; 3) the samples

collected from September to April 1996, with the exception of the aforementioned sample TO1-Jan-96; they are characterised by high concentrations of Ba, Ca, Cr, K, Mg, Mn, Ni and Zn, suggesting a higher input of pollutants during the cold period due to thermal inversion; 4) the samples collected in 2001, with the exception of samples TO1-Dec-01 and TO1-Jan-01, and those collected from May to August 1996; this group is characterised by lower concentrations for all the elements considered, indicating not only the just observed seasonal trend, but also a lower input of pollutants into the atmosphere in the historical centre of Turin in 2001.

Regarding variables, a clear correlation among Ba, Ca, K and Zn is evident, suggesting a common origin due road dust resuspended by the vehicular transportation. This source is usually identified by the combination of elements characterising vehicle exhaust emissions and abrasion of tire and brake linings, such as Ba, Cu, Pb and Zn, along with crustal source elements such as Al, Fe, K, Si, Ti. In particular several researchers (Monaci and Bagagli, 1987; Pakkanen et al. 2001) identified Ba as a marker of road dust source because it is added to lubricating oils to prevent smoke and diesel engine abrasion. Zn in the air near roads is also generated by dust caused by vehicular movement or exhaust emission. The correlation among Cr, Mg and Ni is more difficult to interpret and is likely of anthropogenic origin, possibly due to the transfer of industrial emissions, even if the load in Ni could also suggest a certain contribution from traffic. Ti and Fe are partially correlated with Mn, indicating that a likely source for these elements is soil dust, usually identified by a higher contribution of crustal elements. The correlation between S and Cu could indicate a common source linked to the emissions by power plants and industries. Br, Cl and Pb are neither correlated to each other nor to other elements, confirming their different sources and/or temporal trends. The score and loading plots of the first two principal components for site TO2 are reported in Figure 6a. An interesting trend appears: the samples collected during the cold period are characterised by a greater scattering than those collected during the warm period. In particular the samples collected from September to April 1976, together with some samples collected in November, December and February 1986, form a single cluster aligned with the direction of the vectors representing the main markers of the vehicle exhaust when leaded gasoline was largely used, i.e. Pb and Br. The higher influence of this source during the cold period can be attributed, aside from thermal inversion reported before, to the fact that the transformation of vehicle exhaust into particulate matter is stimulated at low temperature. This is supported by a number of previous studies (e.g. Kittelson et al., 2000; Wehner et al., 2002). A second cluster is formed by the samples collected from September to April 1996 and it is greatly influenced by the variables identified by the vectors of the elements having a more likely crustal origin (Cu, Mg, Mn and Ti), even if the load in Cu could indicate a certain contribution from local traffic and/or industrial emissions transported by wind.

The samples collected from November to March 2001 form a group characterised by high loadings of Ba, Ca, K, Ni and Zn, likely having road dust as a common source, and Cr, widely used as marker for fossil fuel combustion, such as heavy oil inside industrial complexes. Finally the samples collected in the warm periods form two closely-related, but distinct, clusters: the more compact cluster includes the samples collected from May to August 1976 and from March to October 1986 along with sample TO2-Jan-86, whereas the more scattered one is constituted by the samples collected from May to August 1996 and from April to October 2001. Both groups are characterised by low loadings for all the elements, more precisely for Pb and Br in the first cluster and for all other elements, with the exception of S and Cl, in the second cluster. This behaviour further confirms the seasonal trend discussed previously.

The dendrogram (Figure 6b) obtained by Q-mode CA shows that the samples collected in 1976 and 1986 are separated from those collected in 1996 and 2001. It is hence evident that from 1976 to 2001 there was a clear change in the sources influencing the elemental composition of the atmospheric particulate matter in the city of Turin.

#### **4. Conclusions**

Based on the results from this study, several elements including Ba, Cr, Cu, Fe, K, Mn, Pb, Ti and Zn can be quantified on TSP samples with low analysis times using WD-XRF. Routine acquisition of element concentrations in TSP or PM10 samples in many cases would allow the immediate detection of environmental warning situations.

Relatively to the city of Turin, a series of atmospheric particulate matter samples collected over a large number of years is available; this has allowed us to evaluate the temporal trend of the single pollutants in atmospheric PM from this area that likely reflects the changes in the pollutant emissions present in other strongly anthropised areas in the broad time span considered and their possible relationships with changes in typical anthropic activities.

A clear seasonal pattern for element concentrations was noted, with higher levels of all the elements in the cold season. This behaviour is common to that of atmospheric particulate matter in other sites in Northern Italy and it is mainly due to the thermal inversion that occurs in these regions during the winter. Comparing the element seasonal trends from 1976 to 2001, it is evident that the distribution of Br, Cr, Ni, Pb and Zn has changed during the sampling period, particularly between the first (1976 and 1986) and the last (1996 and 2001) two years. This suggests that these elements were emitted into the atmosphere by sources changing with time; more precisely we observed a greater contribution of Pb and Br in the past and a higher level of other pollutants associated with vehicular traffic and industrial activities in the recent years.

The chemometric elaboration of experimental data allowed us to further confirm the seasonal pattern mentioned. Indeed the TSP samples are separated in all PCA plots depending on warm or cold sampling periods rather than on sampling year or site. Moreover, the possible dominant sources influencing the content of the elements studied were hypothesized by PCA and HCA.

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Table 1. Mean, median, minimum and maximum concentrations of each element determined in TSP samples. All values are expressed in  $\text{ng/m}^3$ .

	All the periods				Warm season (April to September)				Cold season (October to March)			
	Mean	Median	Min	Max	Mean	Median	Min	Max	Mean	Median	Min	Max
Ba	6802	6269	23.8	17898	5099	5400	23.8	10149	8400	9062	71.7	17898
Br	8.6	5.7	0.5	31.0	3.8	2.9	0.5	13.8	11.4	7.3	1.6	31.0
Ca	4644	4246	953	14073	3365	2908	953	8540	5923	5175	1362	14073
Cl	628	260	18.6	5752	163	116	18.6	472	1106	621	54.8	5752
Cr	312	323	0.1	1000	213	181	1.9	589	414	387	0.1	1000
Cu	19.2	16.3	1.9	58.2	11.7	10.3	1.9	33.9	27.0	26.7	4.1	58.2
Fe	931	757	34.4	3198	607	471	34.4	1834	1255	1103	82.0	3198
K	1861	1750	122	5385	1352	1185	122	3086	2371	2108	399	5385
Mg	2828	2389	363	9711	1859	1347	432	5358	3796	3323	363	9711
Mn	80.0	71.6	5.6	245	52.3	49.9	5.6	129	106	103	7.8	245
Ni	65.4	63.2	0.4	196	44.8	37.5	1.9	119	85.4	77.0	0.4	196
Pb	53.8	31.66	1.4	350	28.4	24.9	1.4	142	74.0	41.6	7.2	350
S	2497	1690	218	8751	1274	1281	218	3471	3720	3367	391	8751
Ti	78.2	65.2	3.5	366	48.0	33.4	3.5	139	109	103	16.5	366
Zn	356	333	4.9	1056	258	243	4.9	683	454	423	16	1056

## CAPTIONS TO FIGURES

Figure 1. Geographical map of Piedmont and detail of the city of Turin including the areas investigated.

Figure 2. Scatter plots of element concentrations determined by ICP-AES versus XRF.

Figure 3. Temporal trends of element concentrations in TSP samples collected in sites TO1 and TO2: a) Ba, Br, Ca, Cl and Cu; b) Cr, Fe, K, Mg and Mn; c) Ni, Pb, S, Ti and Zn.

Figure 4. Crustal Enrichment Factors (EF) of the elements for: a) 1996 (▲) and 2001 (◇) for site TO1; b) 1976 (■), 1986 (○), 1996 (▲) and 2001 (◇) for site TO2; c) average values for all the years considered (■) for sites TO1 and TO2.

Figure 5. Score and loading plot on PC1-PC2 for site TO1.

Figure 6. Chemometric investigation for site TO2: a) scores and loading plot on PC1-PC2; b) dendrogram obtained by Q-mode CA.

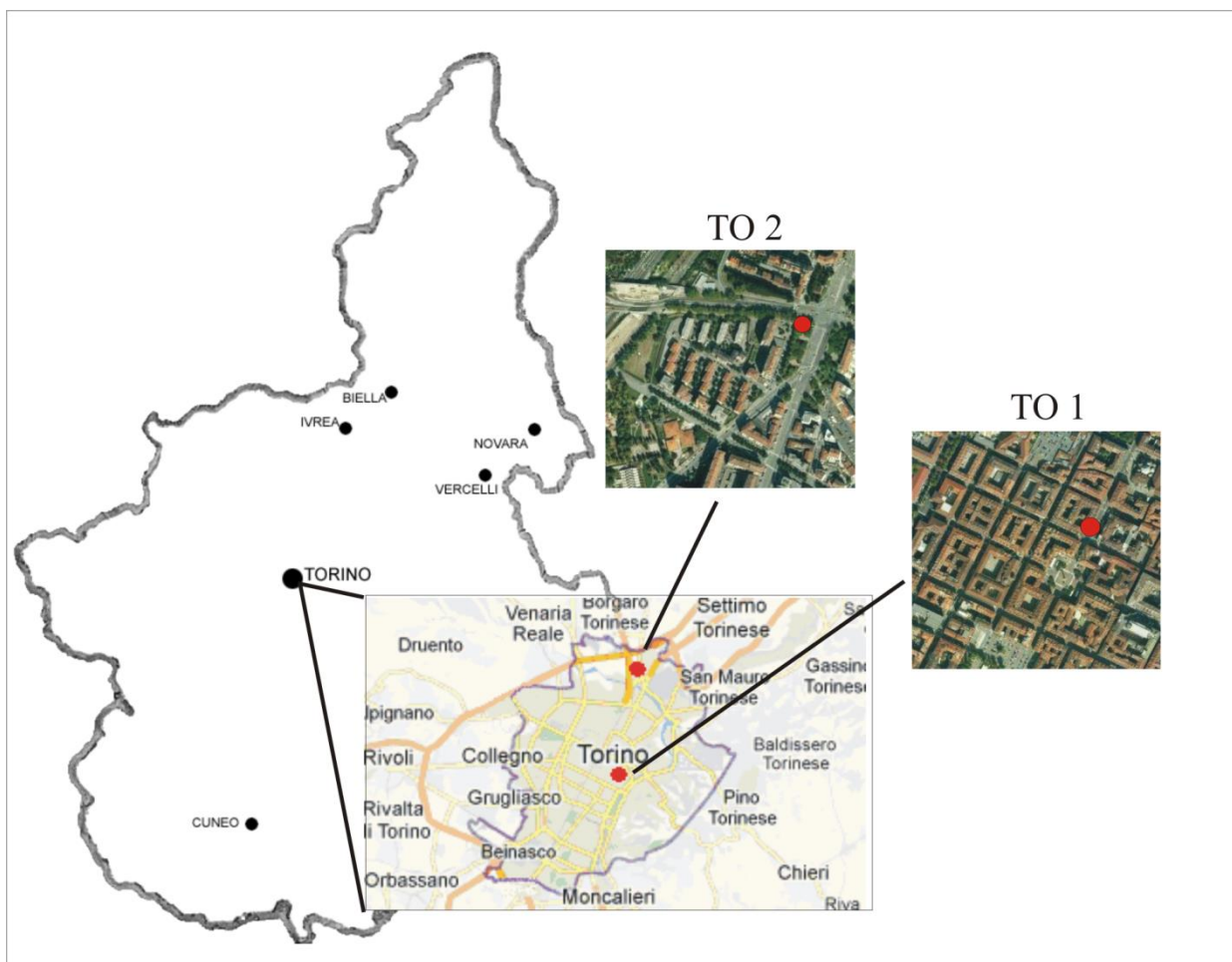


Figure 1

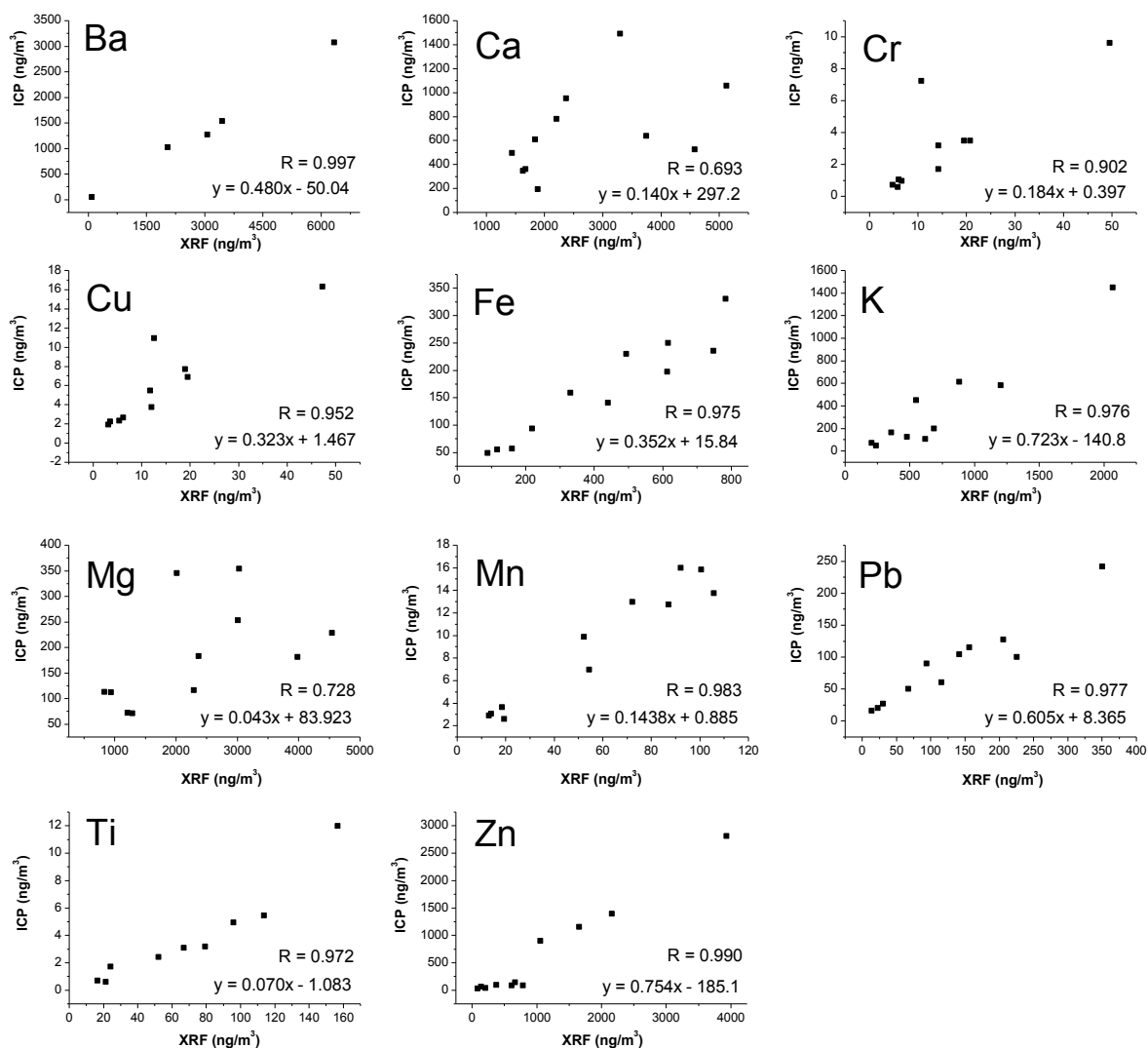
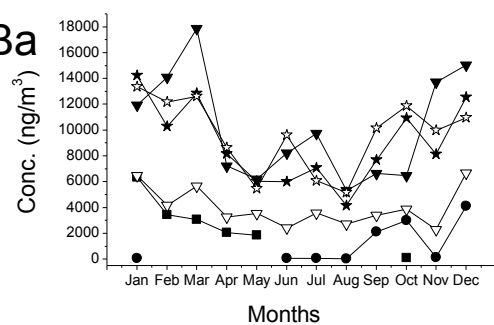


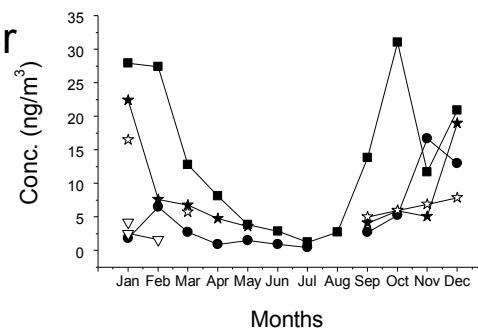
Figure 2

a)

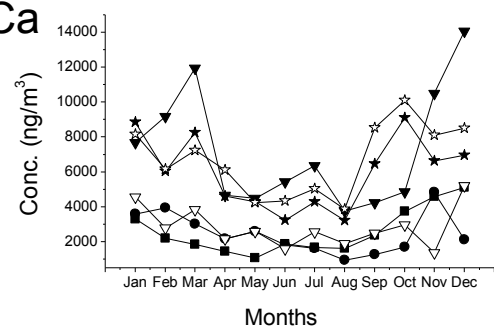
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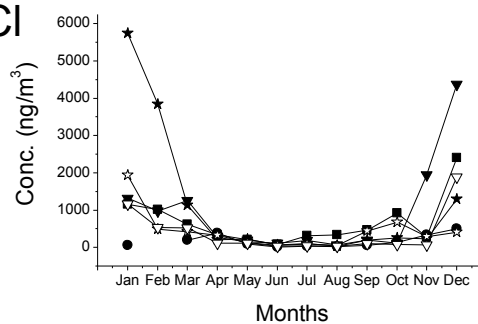
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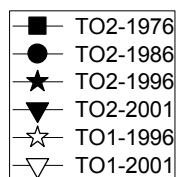
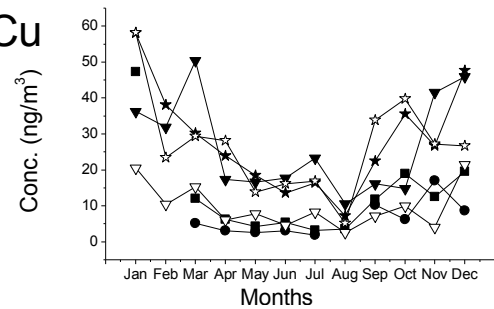
Ca



Cl

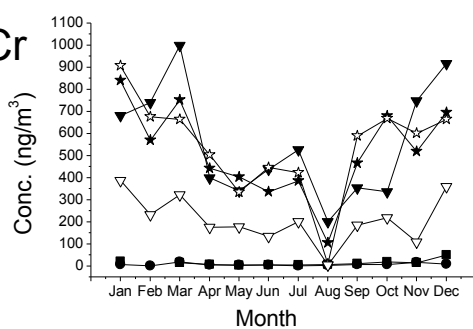


Cu

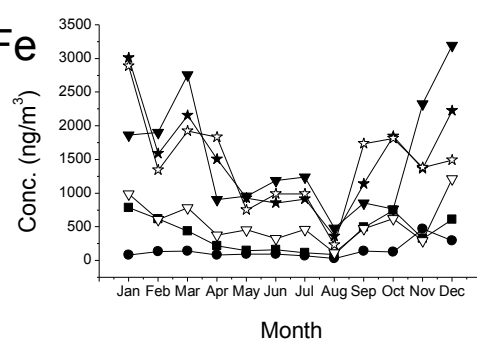


b)

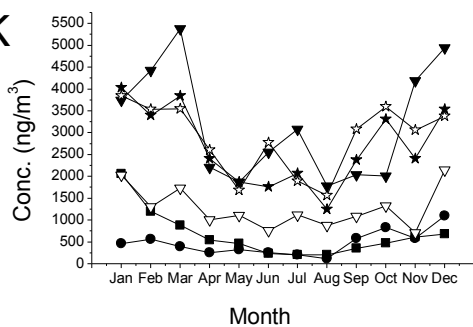
Cr



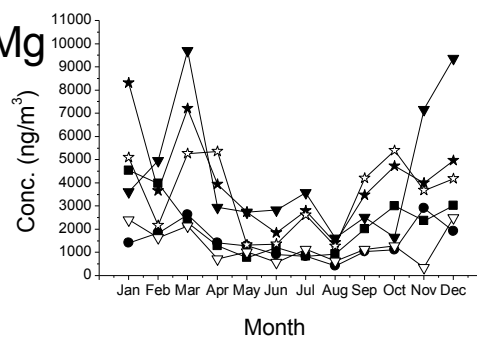
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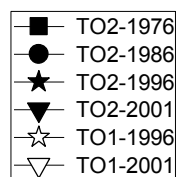
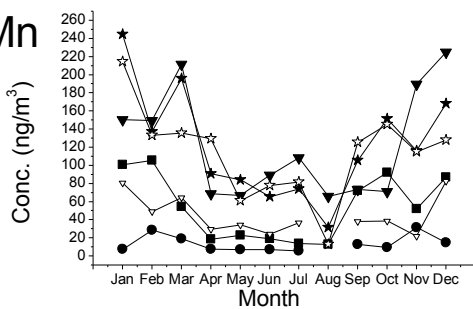
K



Mg



Mn



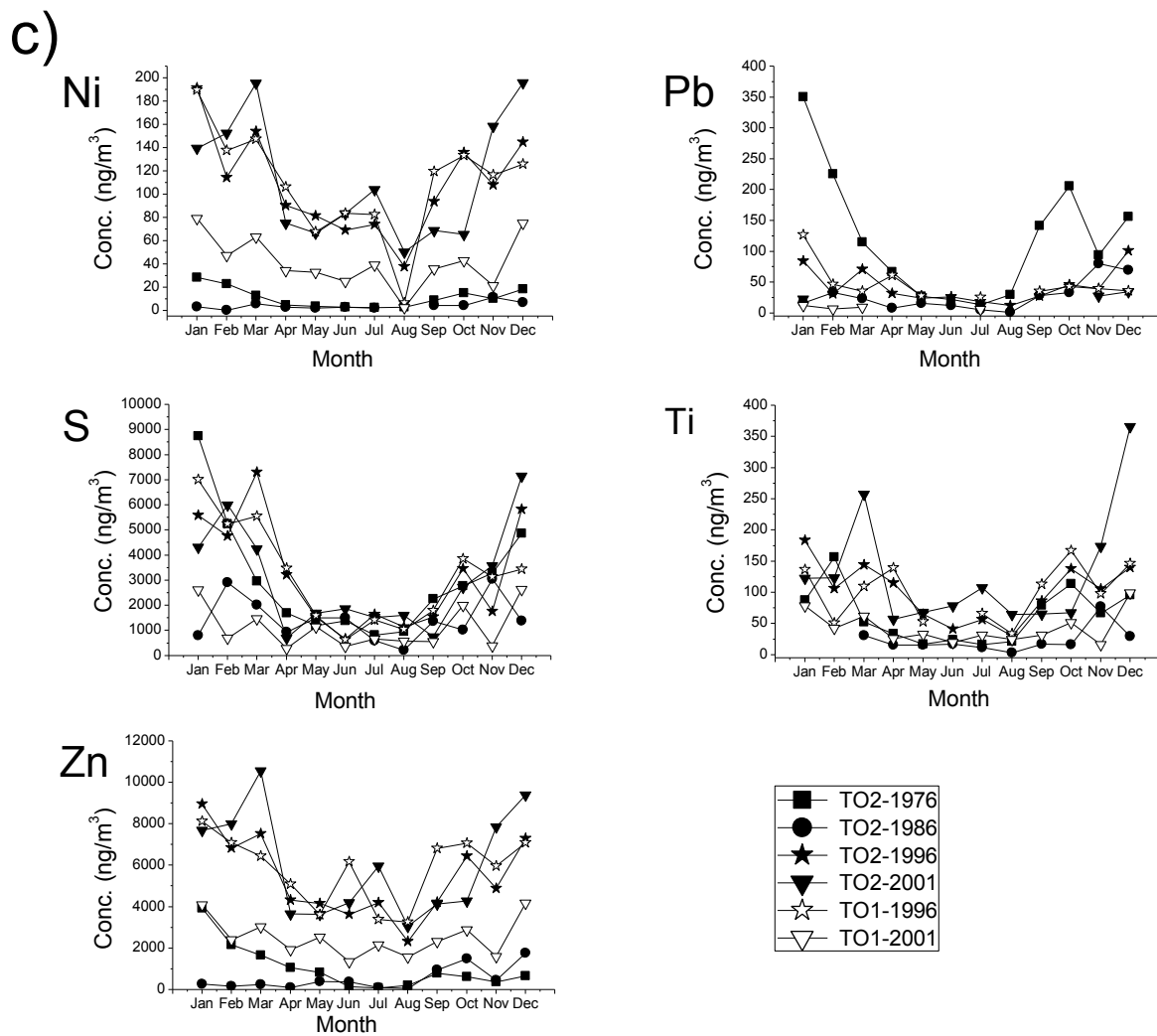


Figure 3

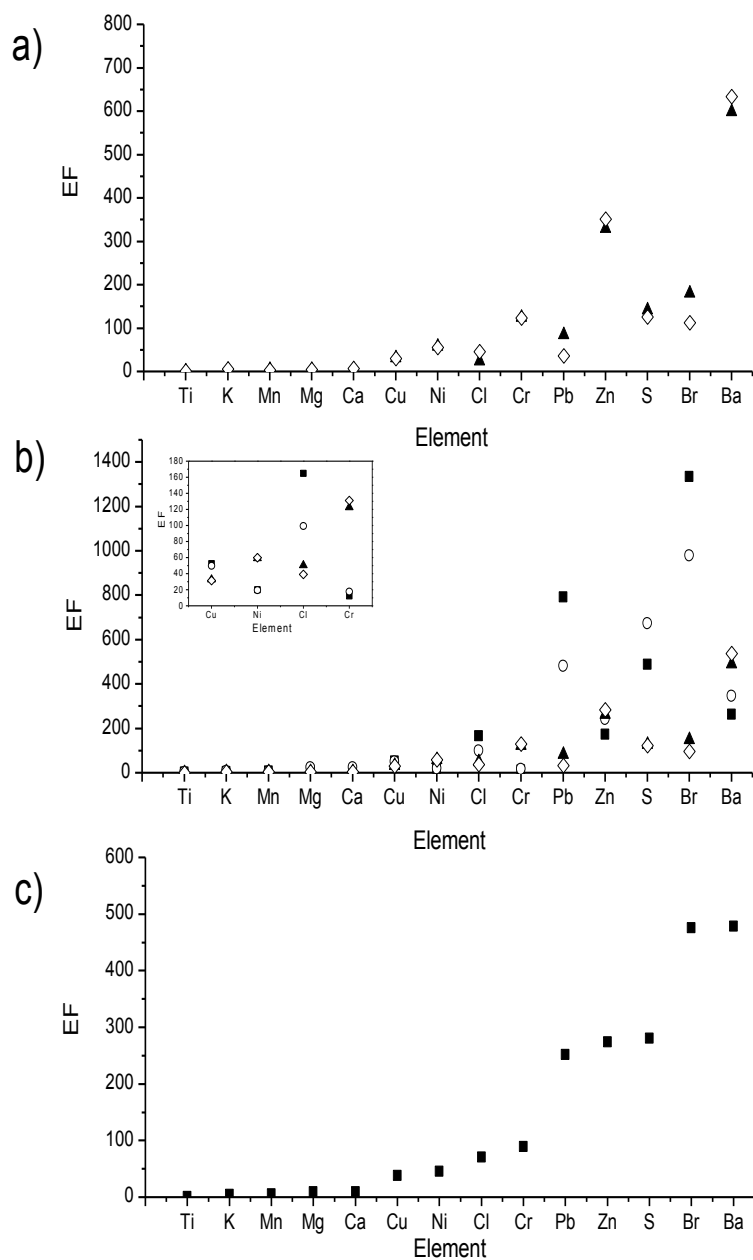


Figure 4



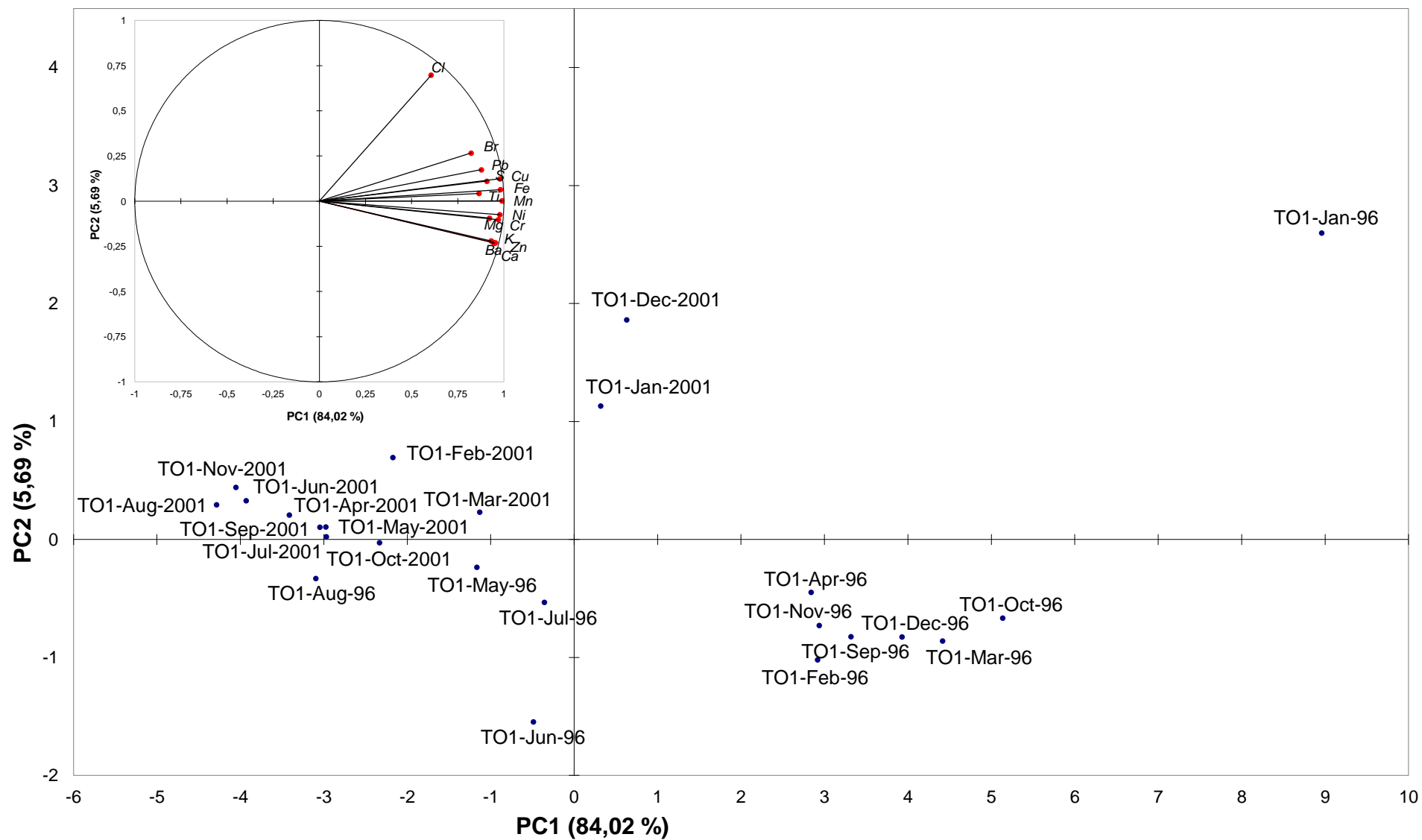
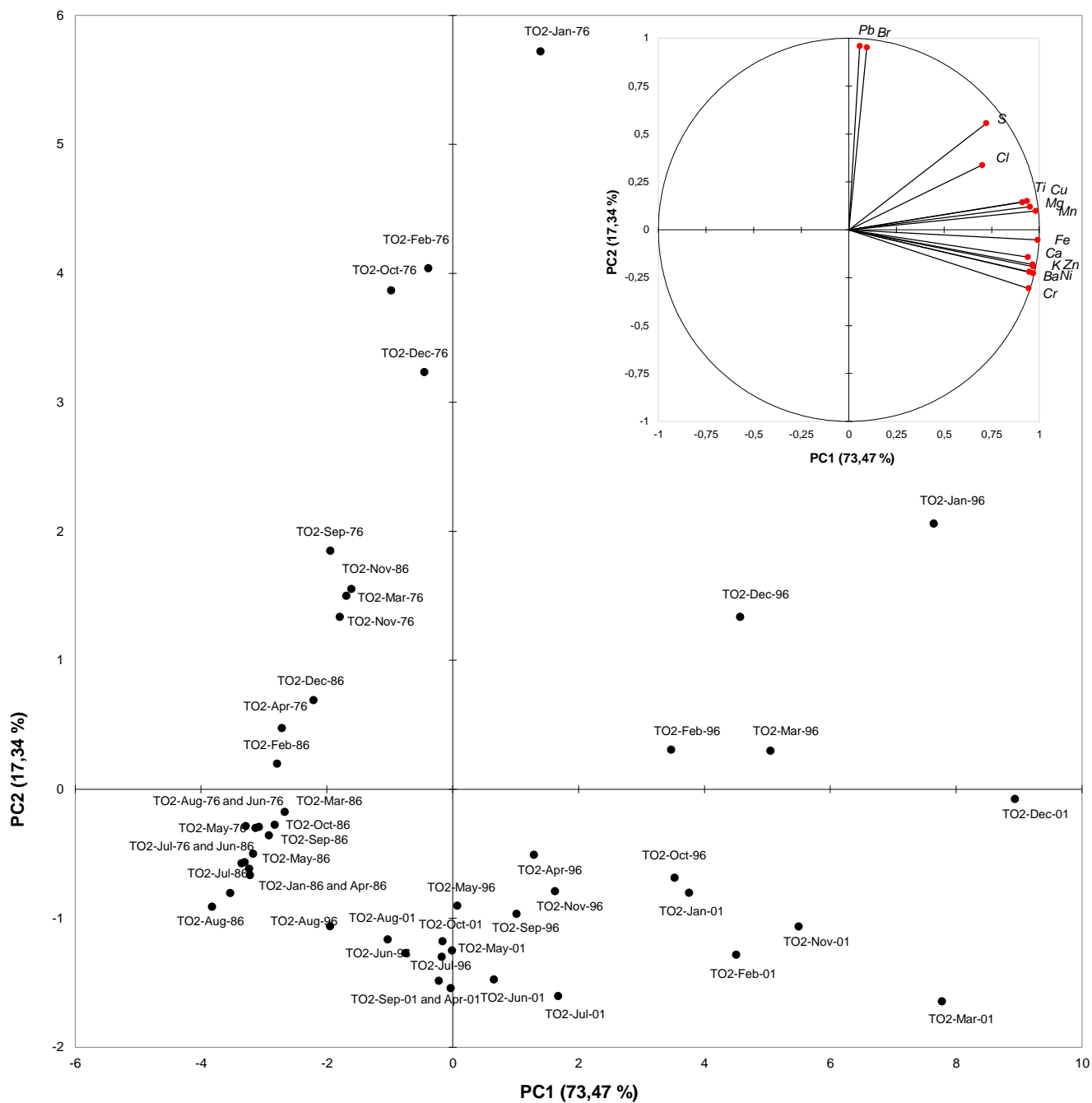


Figure 5

a)



**b)**

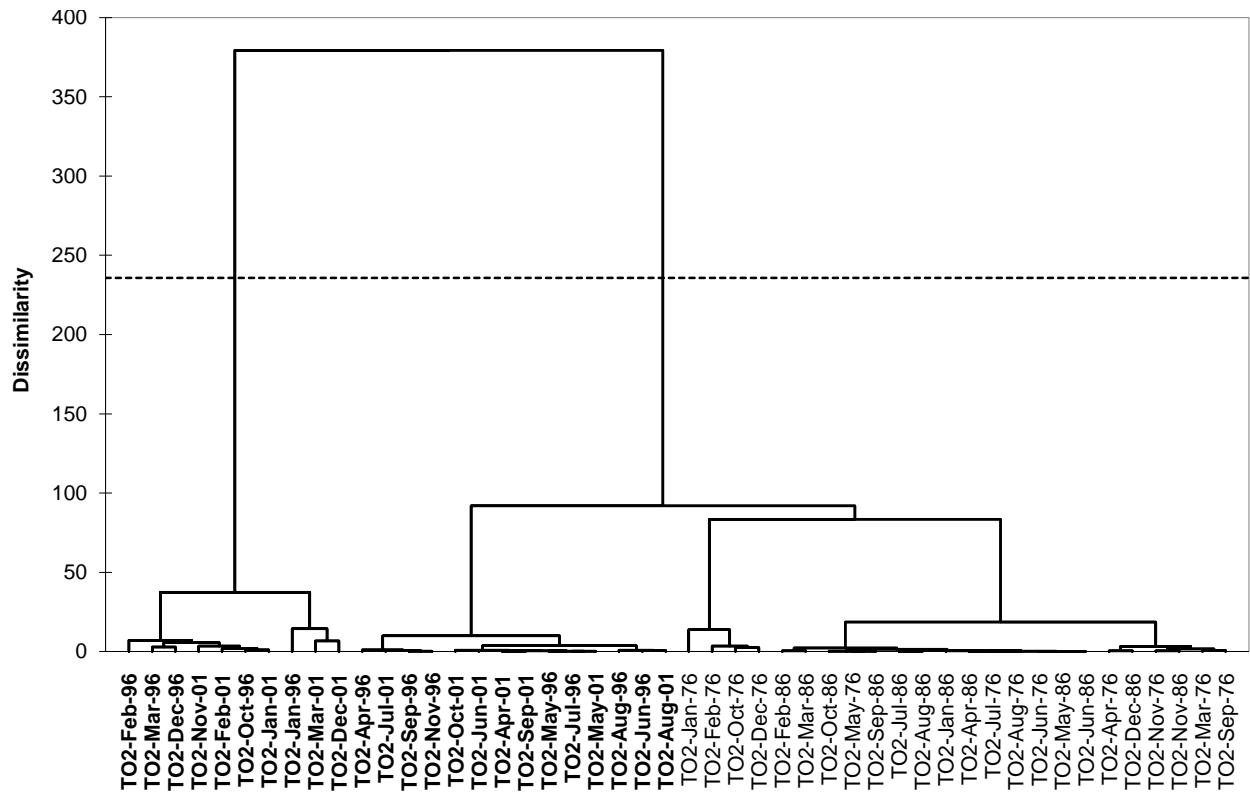


Figure 6